(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 707 057 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
12.01.2000 Bulletin 2000/02

(51) Int Cl.[7]: **C10G 45/58**

(21) Application number: **95305724.7**

(22) Date of filing: **16.08.1995**

(54) Carbon dioxide addition in hydrocracking/hydroisomerization processes to control methane production

Addition von Kohlendioxid in Hydrokrack/Hydroisomerizierungsverfahren zur Kontrolierung der Methanherstellung

Addition de gaz carbonique dans des procédés d'hydrocraquage/hydroisomérisation pour contrôler la production de méthane

(84) Designated Contracting States:
DE FR GB IT NL

(30) Priority: **13.10.1994 US 293362**

(43) Date of publication of application:
17.04.1996 Bulletin 1996/16

(73) Proprietor: **EXXON RESEARCH AND ENGINEERING COMPANY**
Florham Park, New Jersey 07932 (US)

(72) Inventors:
- **Ryan, Daniel Francis**
  Baton Rouge, Louisiana 70820 (US)
- **Wittenbrink, Robert Jay**
  Baton Rouge, Louisiana 70816 (US)

(74) Representative: **Somers, Harold Arnold et al**
ESSO Engineering (Europe) Ltd.
Patents & Licences
Mailpoint 72
Esso House
Ermyn Way
Leatherhead, Surrey KT22 8XE (GB)

(56) References cited:
GB-A- 772 478
US-A- 3 711 399

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 707 057 B1

Printed by Jouve, 75001 PARIS (FR)

BEST AVAILABLE COPY

Description

FIELD OF THE INVENTION

[0001] This invention relates to hydroisomerization processes including hydrocracking wherein the reaction is conducted in the presence of carbon dioxide, and terminal cracking, i.e., methane formation, is substantially minimized without substantial effect on C_2-C_4 yields.

BACKGROUND OF THE INVENTION

[0002] Hydroisomerization processes and catalysts therefor are well known, catalysts including noble metals, Pt, Pd, Rh supported on fluorided alumina, and Group VIII non-noble metals with or without one or more Group VI metals supported on silica, alumina or silica-alumina. These catalysts are usually bifunctional; they contain a metal hydrogenation catalyst and an acidic cracking function.

[0003] Carbon oxides, carbon dioxide and particularly carbon monoxide have have been disclosed in United States Patent No. 3,711,399 as inhibitors of hydrocracking in isomerization processes using highly acidic fluorine containing catalyst, the carbon oxide being added in relatively small amounts. Hydrocracking is virtually completely suppressed and C_4- yields are virtually negligible.

[0004] Hydroisomerization processes produce diesel and jet fuels, and LPG and light hydrocarbon products if the fuels' pour-points are to be appropriate. Methane, however, is a particularly undesirable product since, for example, isomerized products can be made from Fischer-Tropsch waxes which, in turn, ultimately are derived from methane via synthesis gas production. Consequently, there is a requirement for isomerization processes that suppress or substantially eliminate methane formation without substantial effect on LPG and light liquid yields.

SUMMARY OF THE INVENTION

[0005] In accordance with this invention terminal cracking of C_5+ hydrocarbons is substantially suppressed, e.g., to less than about 1.0 weight percent based on feed, by conducting a hydroisomerization process incorporating carbon dioxide in the reaction mixture in the presence of a catalyst comprising one or more Group VIII non-noble metals and one or more Group VI metals, the metals being supported on an acidic support comprising alumina or silica alumina.

[0006] As a consequence of this invention, LPG and light liquid yields are substantially unaffected while methane yield -- resulting from terminal cracking is substantially suppressed. The known literature reports suppression of cracking not only of terminal bonds but also of disubstituted bonds which have a higher activation rate for cracking than terminal bonds. Thus, this invention provides a very selective mechanism for suppressing hydrocracking than the gross operations of the known literature. Further, the literature uses exceedingly low amounts of carbon oxides with highly acidic catalysts. The process of this invention uses greater amounts of carbon dioxide (carbon monoxide not being useful) with a much less acidic catalyst -- a decidedly counter-intuitive approach. As a consequence of this invention LPG yields, e.g., C_2-C_4, and light liquid yields, e.g., C_5-320°F (160°C), 320-500°F (160-260°C) are unaffected while C_1 yields are suppressed to less than about 1 wt%, preferably less than about 0.5 wt%.

DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 shows plots of various product yields when carbon monoxide is added to the feed. Time is always on the abscissa.

[0008] Figures 1a-1f are plots of 700°F+ (371°C+) wax conversion, methane yield, C_2-C_4 yield, C_5-320°F (160°C) yield, 320-500°F (160-260°C) yield, and 500-700°F (260-371°C) yield, all v. time. The first vertical dotted line shows CO in at 320 hours and the second dotted line shows CO out at about 650 hours.

[0009] Figure 2 shows plots of various product yields when carbon dioxide is added to the feed. Time is always on the abscissa.

[0010] Figures 2a-2f show yields for the same products as in Figures 1a-1f. The dotted line shows CO_2 in at about 320 hours.

[0011] The amount of carbon dioxide used in conjunction with feed is at least about 0.2 mole % based in feed, preferably at least about 0.3 mole %, preferably 0.3 mole % to 1.0 mole %. Of interest is the fact that while carbon oxides are often lumped together as catalyst poisons, only carbon dioxide suppressed terminal cracking with the non-noble metal, functional catalyst of this invention; carbon monoxide had virtually no effect on the process.

[0012] Total conversion of feed during the process is 20-90%, preferably 30-70%, and more preferably 40-60%.

[0013] The active hydroisomerization metals are non-noble metals selected from Group VIII of the Periodic chart of the Elements. Preferred metals are nickel and cobalt or mixtures thereof and mixtures thereof with molybdenum, a

Group VI metal. The Group VIII metals may be present on the catalyst in amounts sufficient to be catalytically active for hydroisomerization. Specifically, metal concentrations ranging from 0.05 to 20 wt%, preferably 0.1 to 10 wt%, still more preferably 2.0 to 5.0 wt% may be used. For example, in a preferred catalyst the cobalt loading may be 1-4 wt%, and the nickel loading may be 0.1-1.5 wt%. A Group VI metal such as molybdenum is also employed in amounts more or less than or equal to the non-noble Group VIII metal, e.g., 1.0 to 20 wt%, preferably 8-15 wt%, in all cases by total weight of catalyst.

[0014] The metals are impregnated onto or added to the support as suitable metal salts or acids, e.g., nickel or cobalt nitrate, etc. The catalyst is then dried and calcined in well known fashions.

[0015] The base silica and alumina materials used in this invention may be, for example, soluble silicon containing compounds such as alkali metal silicates (preferably where $Na_2O:SiO_2$=1:2 to 1:4), tetraalkoxysilane, orthosilicic acid ester, etc.; sulfates, nitrates, or chlorides of aluminum alkali metal aluminates, or inorganic or organic salts of alkoxides or the like. When precipitating the hydrates of silica or alumina from a solution of such starting materials, a suitable acid or base is added and the pH is set within the range of about 6.0 to 11.0. Precipitation and aging are carried out, with heating, by adding an acid or base under reflux to prevent evaporation of the treating liquid and change of pH. The remainder of the support producing process is the same as those commonly employed, including filtering, drying and calcination of the support material. The support may also contain small amounts, e.g., 1-30 wt% of materials such as magnesia, titania, zirconia, hafnia, or the like.

[0016] A preferred support is an amorphous silica-alumina carrier, containing less than about 35 wt% silica, preferably about 2-35 wt% silica, more preferably 5 to 30 wt% silica, and having the following pore-structural characteristics:

Pore Radius (A)	Pore Volume
0-300	>0.03 ml/g
100-75,000	<0.35 ml/g
0-30	<25% of the volume of the pores with 0-300 A radius
100-300	<40% of the volume of the pores with 0-300 A radius

[0017] Such materials and their preparation are described more fully in U.S. Patent No. 3,843,509. The materials have a surface area ranging from about 180-400 m^2g, preferably 230-375 m^2/g, a pore volume of 0.3 to 1.0 ml/g, preferably 0.5 to 0.95 ml/g, bulk density of about 0.5-1.0 g/ml, and a side crushing strength of about 0.8 to 3.5 kg/mm.

[0018] The feed materials that are isomerized with the catalyst of this invention are waxy feeds, i.e., C_5+, preferably boiling above about 350°F (177°C) preferably above about 550°F (288°C) and may be obtained either from a Fischer-Tropsch process which produces substantially normal paraffins or from slack waxes. Slack waxes are the by-products of dewaxing operations where a diluent such as propane or a ketone (e.g., methylethyl ketone, methyl isobutyl ketone) or other diluent is employed to promote wax crystal growth, the wax being removed from the lubricating oil base stock by filtration or other suitable means. The slack waxes are generally paraffinic in nature, boil above about 600°F (316°C), preferably in the range of 600°F (316°C) to about 1050°F (566°C), and may contain from 1 to 35 wt% oil. Waxes with low oil contents, e.g., 5-20 wt% are preferred; however, waxy distillates or raffinates containing 5-45% wax may also be used as feeds. Slack waxes are usually freed of polynuclear aromatics and heteroatom compounds by techniques known in the art, e.g., mild hydrotreating as described in U.S. Patent No. 4,900,707, which also reduces sulfur and nitrogen levels preferably to less than 5 ppm and less than 2 ppm, respectively. Fischer-Tropsch waxes are preferred feed materials, having negligible amounts of aromatics, sulfur and nitrogen compounds.

[0019] Isomerization conditions usually include temperatures of 300-400°C, 3.54 - 20.78 MPa (500-3000 psig) hydrogen, 237.5 - 2375 litres/litre (1000-10,000 SCF/bbl) hydrogen treat and space velocity of 0.1-10.0 LHSV. Preferred conditions include 320-385°C, 5,27 - 10,44 MPa (750-1500 psig) hydrogen, 0.5-2 v/v/hr.

[0020] The catalyst is generally employed in a particulate form, e.g., cylindrical extrudates, trilobes, quadrilobes, and ranging in size from about 1-5 mm. The hydroisomerization can be carried out in a fixed bed reactor and the products may be recovered by distillation.

[0021] The following examples will illustrate this invention but are not meant to be limiting in any way.

[0022] All of the hydroisomerization studies were carried out in a small upflow pilot plant. The catalyst was evaluated at 5.27 MPa (750 psig), 0.50 LHSV, 690-700°F (366-377°C), and with a nominal H_2 treat rate of 593.7 litres/litre (2500 SCF/B). A 10 cc charge of catalyst crushed and sized to 14/35 mesh was employed in each case. The catalyst comprised 15.2 wt% MoO_3 and 3.2 wt% CoO on a silica-alumina Co gel with 20-30 wt% bulk silica. Balances were typically collected at 24-72 hour intervals. The reaction temperature was set to meet a target of 50% 700°F+ wax conversion and was not adjusted during the run. The Fischer-Tropsch wax employed in these studies had a nominal composition of 0.70% IBP-500°F (260°C), 20.48% 500-700°F (260-371°C), 78.82% 700°F+ (371°C). Typical run lengths were 800-1000 hours. Boiling range distributions for gas, naphtha, distillate range products, and lubes were obtained by a

combination of simulated gas chromatography distillation and gas chromatography-mass spectroscopy.

[0023] The effect of carbon monoxide was evaluated and the catalyst was activated using the following procedure:

1. Pressure test at 100°F (38°C) at ca. 5.17 MPa (750 psi) hydrogen pressure.

2. Reactor temperature increased to 700°F (371°C) while maintaining hydrogen pressure at 5.17 MPa (750 psi) and a flow rate of 593.7 litres/litre (2500 SCF/bbl).

3. Reactor temperature held at 700°F (371°C) for approximately 18 hours.

4. Hydrogen feed and pressure were adjusted to standard operating conditions and feed was cut in feed to start operation.

[0024] After feed was cut in, balances were collected on a regular basis for 16 days to ensure that the catalyst had lined out, i.e., reached steady state conditions. At this point, the gas was switched from pure hydrogen to a mixture containing 0.405 mole % carbon monoxide in a balance of hydrogen. After 13 days on the CO/H_2 mixture, the gas was switched back to pure hydrogen for the remainder of the run.

[0025] In this case there was an increase in C_1 (methane), likely due to the hydrogenation of CO under reaction conditions.

[0026] The effect of carbon dioxide was studied also. In this case a somewhat different but similar catalyst activation procedure was used and is outlined below. This activation procedure leads to high methane yields.

1. Reactor temperature increased to 250°F (121°C) at atmospheric pressure under nitrogen.

2. Pressure test with nitrogen, followed by pressure test with hydrogen, while maintaining reactor temperature at 250°F (121°C).

3. Reactor pressure increased to 1250 psia with hydrogen flow rate at 807.4 litres/litre (3400 SCF/B). Reactor temperature increased at a rate of 30°F (16°C) per hour to 700°F (371°C). Once reactor temperature reaches 700°F (371°C), hold for approximately 4-5 hours.

4. Pressure test hot with hydrogen; reduce hydrogen feed and pressure to standard operating conditions; cut in feed to start operation.

[0027] As in the previous run, once feed was cut-in balances were collected on a regular basis for 13.5 days to ensure that the catalyst had lined out. At this point the gas was switched from pure hydrogen to a mixture of 0.604 mole % carbon dioxide, the balance being hydrogen for the remainder of the run.

[0028] The effect of carbon monoxide on the catalyst performance is displayed graphically in Figure 1. In general, the CO seemed to have very little impact on the catalyst performance. The most significant effect was a decrease in the 700°F+ (371°C+) wax conversion which was observed almost immediately after the CO was introduced. This decrease continued until the conversion leveled off at about 55 percent and stayed at this level even when pure hydrogen was reintroduced to the system.

[0029] A small change in the methane yield was also detected. The methane yield actually increased when the CO was introduced. This occurred even though the conversion level was decreasing. Generally, methane yield tracks reasonably well with conversion (i.e., an increase in conversion usually leads to an increase in methane). However, in this case, the slight increase in methane yield may be due to CO hydrogenation, particularly since the methane level drops significantly when pure hydrogen is reintroduced and corresponds almost exactly with the amount of methane which would be produced if the CO was quantitatively converted to methane.

[0030] Examination of the remaining products (e.g., C_2-C_4, C_5-320°F (160°C), 320-500°F (160-260°C), 500-700°F (260-371°C)) reveal little or no effect from the CO other than differences attributed to the change in conversion.

[0031] The effect of carbon dioxide on the catalyst performance is displayed graphically in Figure 2. Although the product selectivities for this run are significantly different than those obtained in the CO experiment (primarily due to the different activation procedures), it is the relative effect of the CO_2 that is of primary importance.

[0032] Shortly after the introduction of the CO_2/H_2 mixture, the 700°F+ (371°C+) wax conversion decreased by about 17%. The conversion slowly started to increase thereafter but did not reached the original level.

[0033] The methane yield shows the most dramatic change as a result of the CO_2. The activation procedure used in this run caused an extremely high methane yield of about 2 wt%. Introduction of CO_2 caused this level to drop to less than 0.30 wt% where it remained for the duration of the run. A small reduction in the methane yield would be

expected due to the decrease in the conversion; however, the effect is too great to account for the total reduction.

[0034] Examination of the remaining products (e.g., C_2-C_4, C_5-320°F (160°C), 320-500°F (160-260°C), 500-700°F (260-371°C) reveal little or no effect from the CO_2 other than differences attributed to the changes in conversion.

[0035] The following table illustrates the actual product yields for the CO_2 experiment.

Total Time On Run (Hours)	297.0	320.5	434.0	650.0	770.5
Delta Time	-----	t=0	t=113.5	t=329.5	t=450
700°F+ Conversion	46.88	52.12	41.64	40.67	45.71
CH_4	2.005	2.022	0.265	0.256	0.237
C_2H_6	0.196	0.190	0.033	0.037	0.043
C_3H_8	0.416	0.414	0.358	0.408	0.472
C_4H_{10}	1.140	1.182	1.054	1.289	1.555
t = 0 is the point at which carbon dioxide was added					

These data were taken after line-out had been achieved.

[0036] From the table it is clear that C_1 (methane) was substantially suppressed; C_2 was suppressed somewhat, C_3 and C_4 were virtually unaffected and as a result C_2-C_4 was substantially unaffected. Additionally, total conversion was suppressed at the outset of CO_2 addition, and recovered somewhat as the reaction proceeded. Thus, C_2-C_4 cracked products can range from about 1 wt% to about 3 wt%.

Claims

1. A process for suppressing CH_4 yield in the hydroisomerization of C_{5+} paraffinic feed which comprises contacting the feed at hydroisomerization conditions with a catalyst comprising a non-noble Group VIII metal component and a Group VI metal component supported on alumina or silica-alumina and in the presence of hydrogen and at least 0.2 mol % carbon dioxide based on feed.

2. The process of claim 1 wherein the carbon dioxide is present in amounts in the range of 0.3 to 1.0 mole %.

3. The process of claim 1 or claim 2 wherein the catalyst contains at least one Group VIII non-noble metal oxide and at least one Group VI metal oxide.

4. The process of any one of claims 1 to 3 wherein a Group VIII metal of the catalyst is cobalt and a Group VI metal of the catalyst is molybdenum.

5. The process of any one of claims 1 to 4 wherein the support is a silica-alumina support and the silica is less than about 35 wt% of the support.

6. The process of any one of claims 1 to 5 wherein the support contains from 2-30 wt% silica.

7. The process of any one of claims 1 to 6 wherein the surface area of the support is in the range of from 180-400 m^2/gm.

8. The process of any one of claims 1 to 7 wherein the total conversion of the feed is in the range of from 30-70%.

9. The process of any one of claims 1 to 8 comprising recovering from the catalytic hydroisomerization step an isomerized product having a methane content of less than about 1 wt% on feed.

10. The process of any one of claims 1 to 9 wherein the feed boils at temperatures above 550°F (288°C).

11. The process of any one of claims 1 to 10 wherein the isomerization conditions include a temperature in the range of from 300 to 400°C.

Patentansprüche

1. Verfahren zum Unterdrücken der CH_4-Ausbeute bei der Hydroisomerisierung von paraffinischem C_{5+}-Einsatzmaterial, bei dem das Einsatzmaterial bei Hydroisomerisierungsbedingungen mit Katalysator, der eine Nicht-Edelmetallkomponente der Gruppe VIII und eine Gruppe VI Metallkomponente auf einem Träger aus Aluminiumoxid oder Siliciumdioxid-Aluminiumoxid umfaßt, und in Gegenwart von Wasserstoff und mindestens 0,2 Mol.% Kohlendioxid, bezogen auf das Einsatzmaterial, kontaktiert wird.

2. Verfahren nach Anspruch 1, bei dem das Kohlendioxid in Mengen im Bereich von 0,3 bis 1,0 Mol.% vorhanden ist.

3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem der Katalysator mindestens ein Nicht-Edelmetalloxid der Gruppe VIII und mindestens ein Gruppe VI Metalloxid enthält.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem ein Gruppe VIII Metall des Katalysators Kobalt ist und ein Gruppe VI Metall des Katalysators Molybdän ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem der Träger ein Siliciumdioxid-Aluminiumoxid-Träger ist und das Siliciumdioxid weniger als etwa 35 Gew.% des Trägers ausmacht.

6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem der Träger 2 bis 30 Gew.% Siliciumdioxid enthält.

7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem die Oberfläche des Trägers im Bereich von 180 bis 400 m^2/g liegt.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem die Gesamtumwandlung des Einsatzmaterials im Bereich von 30 bis 70 % liegt.

9. Verfahren nach einem der Ansprüche 1 bis 8, bei dem aus der katalytischen Hydroisomerisierungsstufe isomerisiertes Produkt mit einem auf das Einsatzmaterial bezogenen Methangehalt von weniger als etwa 1 Gew.% gewonnen wird.

10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem das Einsatzmaterial bei Temperaturen über 288°C (550°F) siedet.

11. Verfahren nach einem der Ansprüche 1 bis 10, bei dem die Isomerisierungsbedingungen eine Temperatur im Bereich von 300 bis 400°C einschließen.

Revendications

1. Procédé de suppression du rendement en CH_4 dans l'hydroisomérisation d'une charge d'alimentation paraffinique en C_{5+}, qui comprend la mise en contact de la charge d'alimentation dans des conditions d'hydroisomérisation avec un catalyseur comprenant un composant de métal non noble du groupe VIII et un composant de métal du groupe VI sur de la silice ou de la silice-alumine et en présence d'hydrogène et d'au moins 0,2% en mole de dioxyde de carbone par rapport à la charge d'alimentation.

2. Procédé selon la revendication 1, dans lequel le dioxyde de carbone est présent en quantités dans la plage de 0,3% à 1,0% en mole.

3. Procédé selon la revendication 1 ou 2, dans lequel le catalyseur contient au moins un oxyde de métal non noble du groupe VIII et au moins un oxyde de métal du groupe VI.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le métal du groupe VIII du catalyseur est le cobalt et le métal du groupe VI du catalyseur est le molybdène.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le support est un support de silice-alumine et la silice est présente en quantité inférieure à environ 35% en poids du support.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le support contient 2-30% en poids de silice.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la surface spécifique du support se situe dans la plage de 180-400 m^2/g.

8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel la conversion totale de la charge d'alimentation se situe dans la plage de 30-70%.

9. Procédé selon l'une quelconque des revendications 1 à 8, comprenant la récupération à l'étape d'hydroisomérisation catalytique d'un produit isomérisé ayant une teneur en méthane de moins d'environ 1% par rapport à la charge d'alimentation.

10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel la charge d'alimentation bout à des températures supérieures à 288°C (550°F).

11. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel les conditions d'isomérisation comprennent une température dans la plage de 300°C à 400°C.

FIGURE 1a

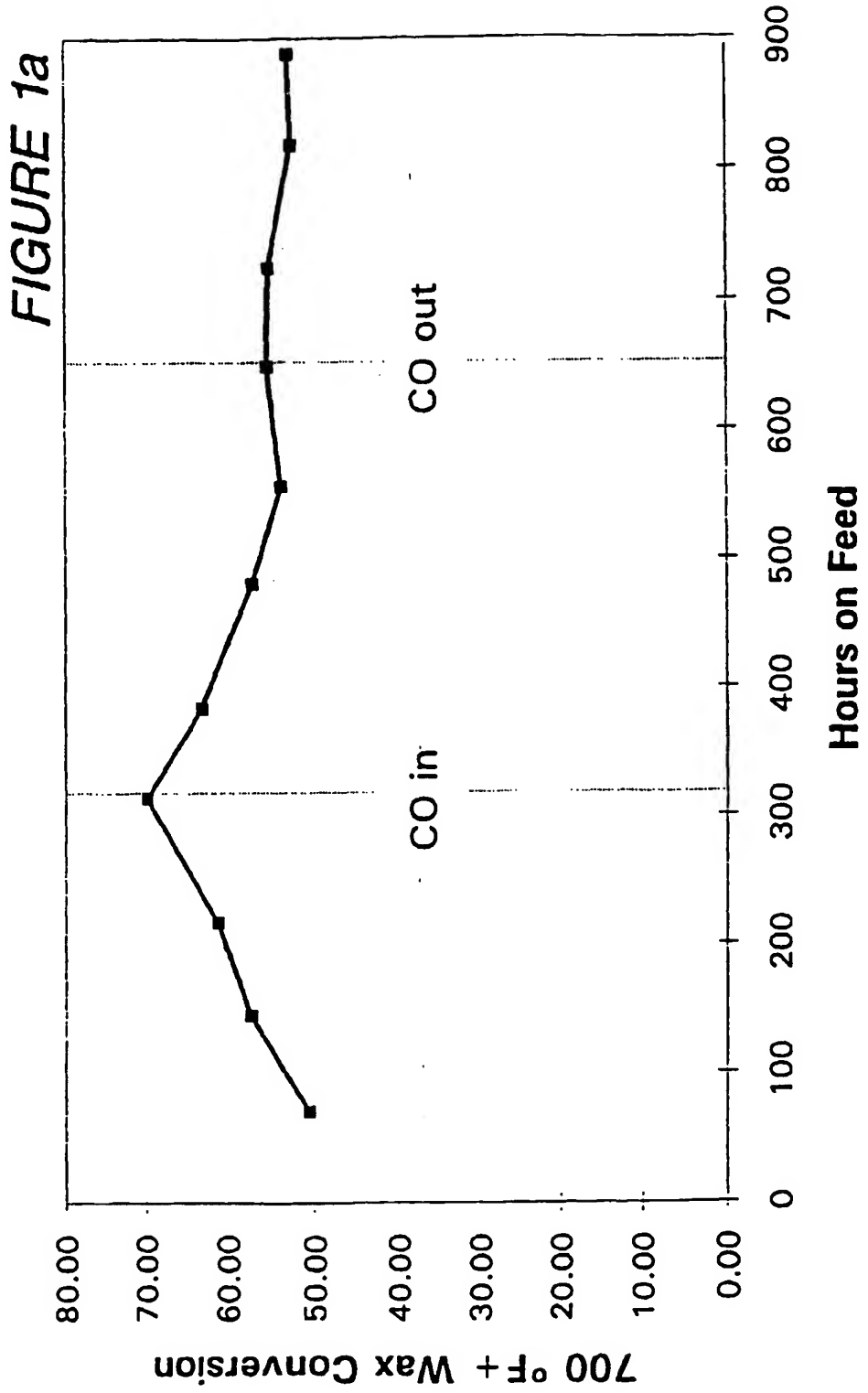

700 °F+ Wax Conversion
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0
100
200
300
400
500
600
700
800
900
Hours on Feed
CO in
CO out

FIGURE 1b

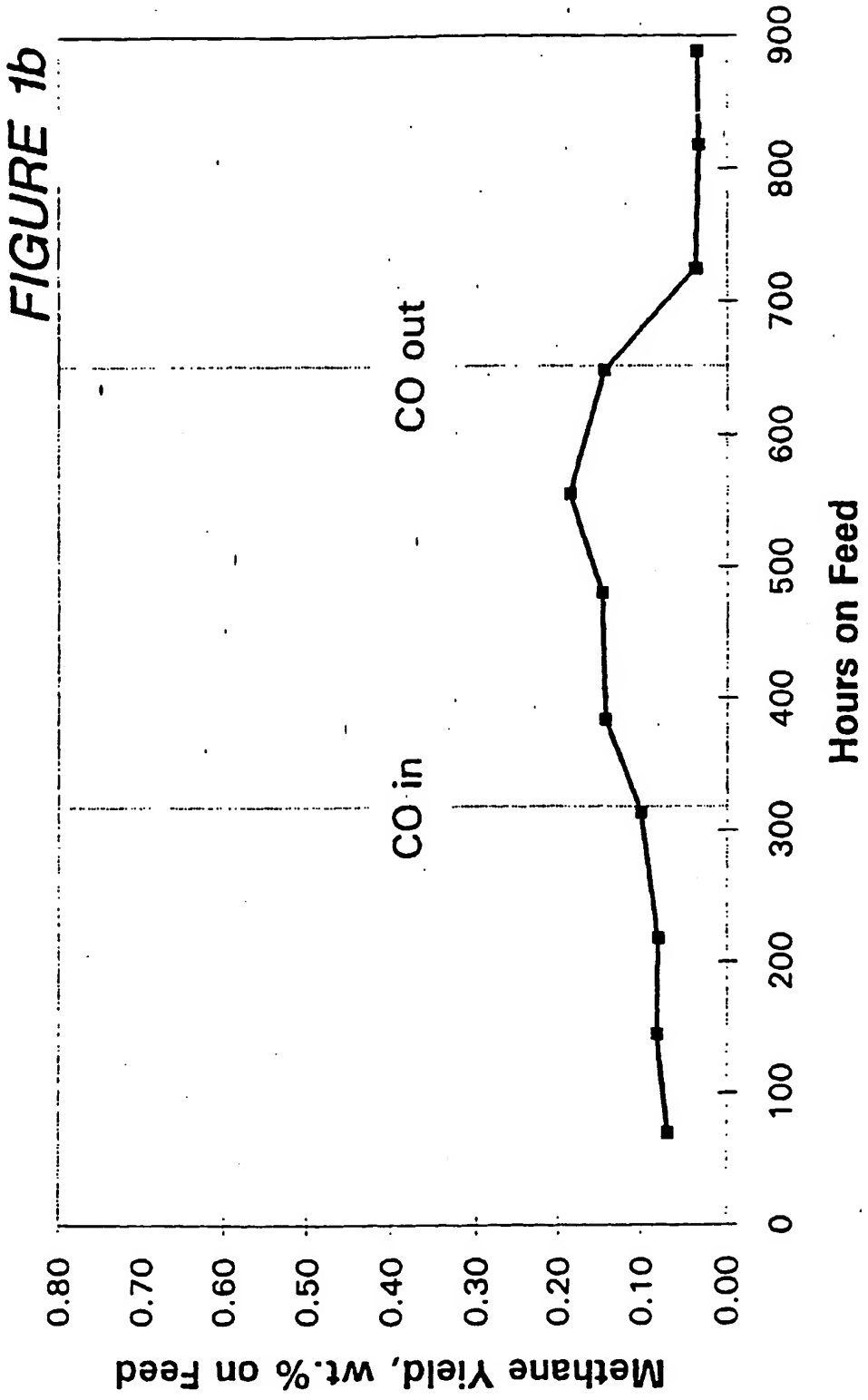

Methane Yield, wt.% on Feed
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
100
200
300
400
500
600
700
800
900
Hours on Feed
CO in
CO out

FIGURE 1c

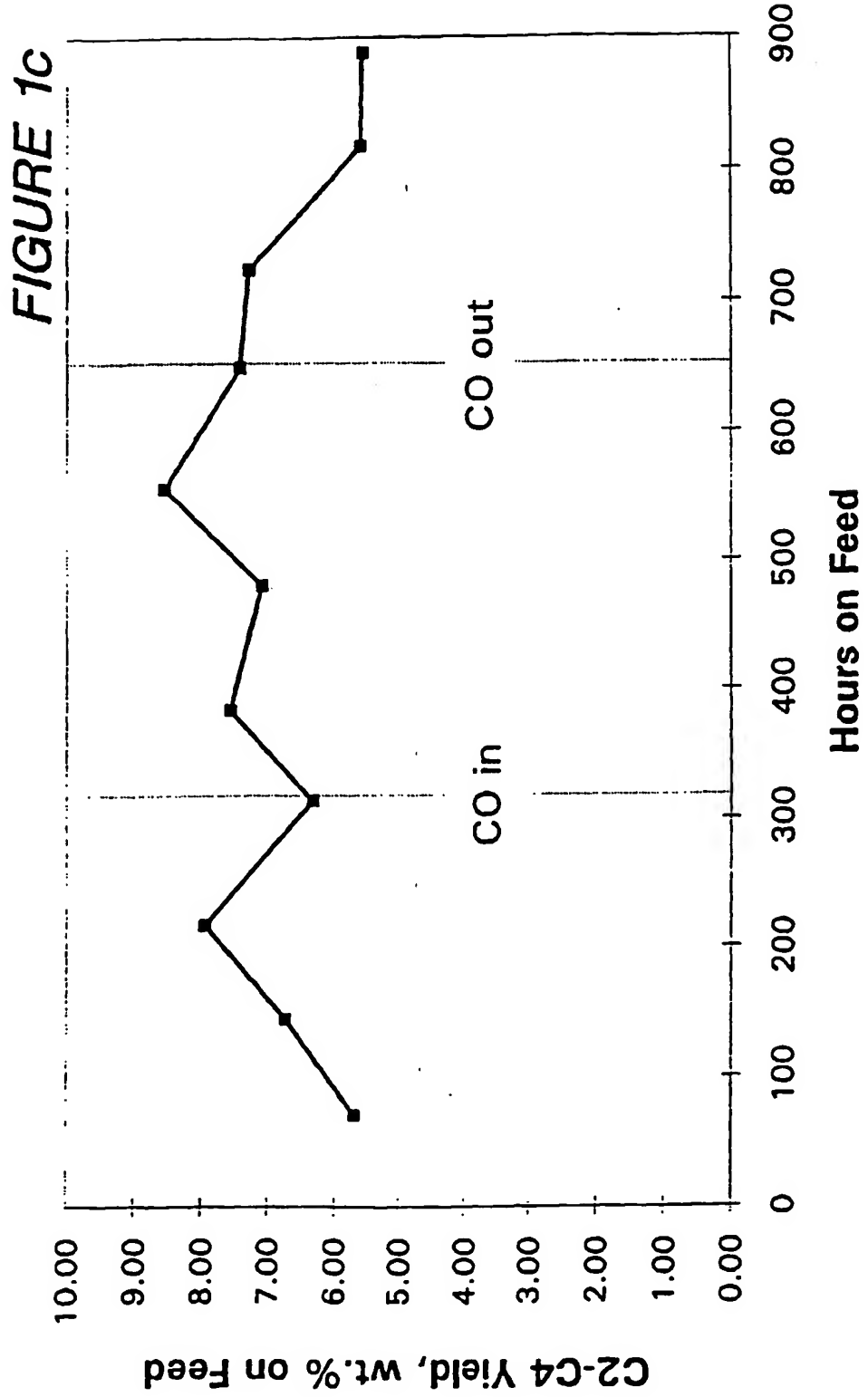

C2-C4 Yield, wt.% on Feed
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0
100
200
300
400
500
600
700
800
900
Hours on Feed
CO in
CO out

FIGURE 1d

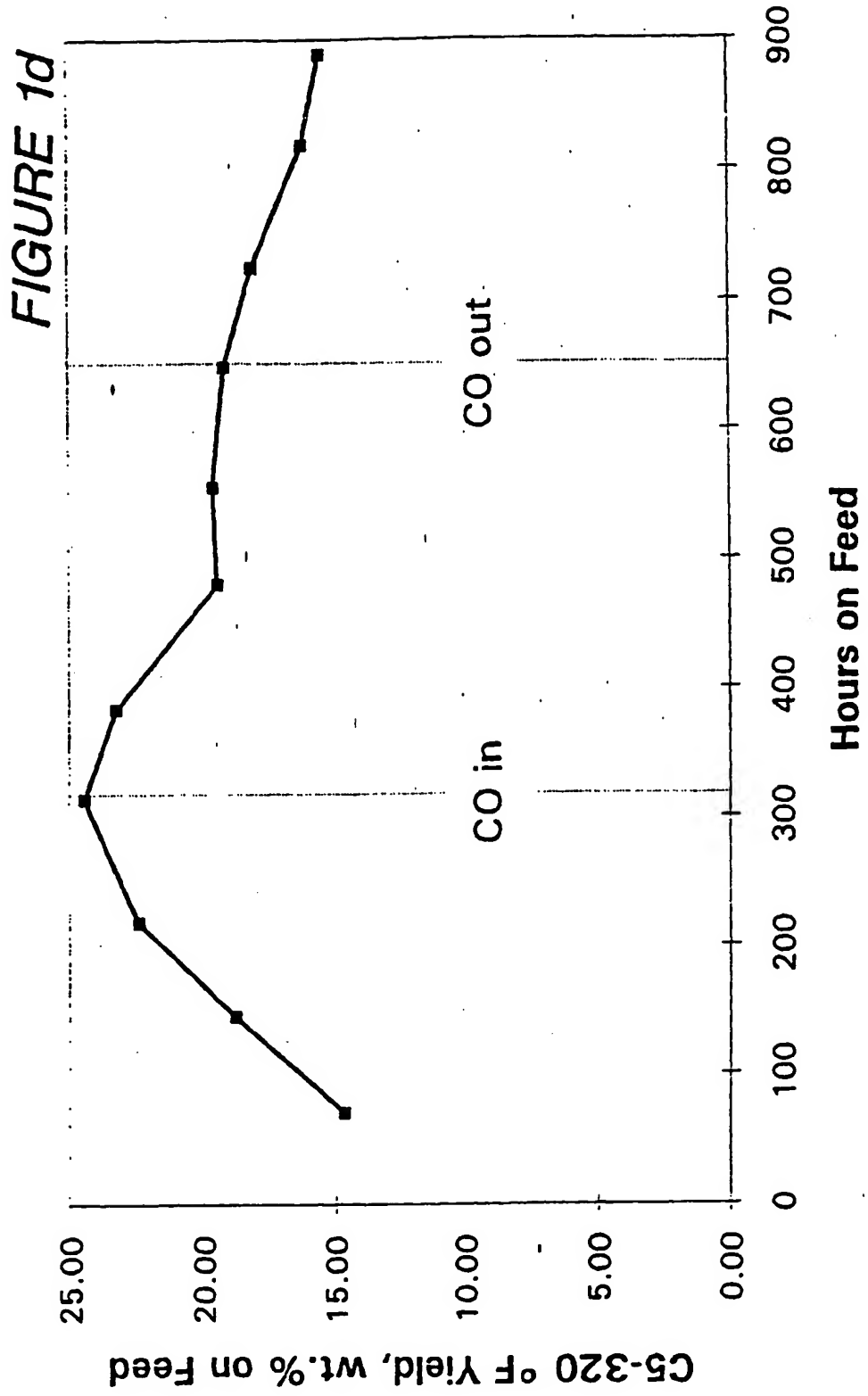

C5-320 °F Yield, wt.% on Feed
25.00
20.00
15.00
10.00
5.00
0.00
0
100
200
300
400
500
600
700
800
900
Hours on Feed
CO in
CO out

FIGURE 1e

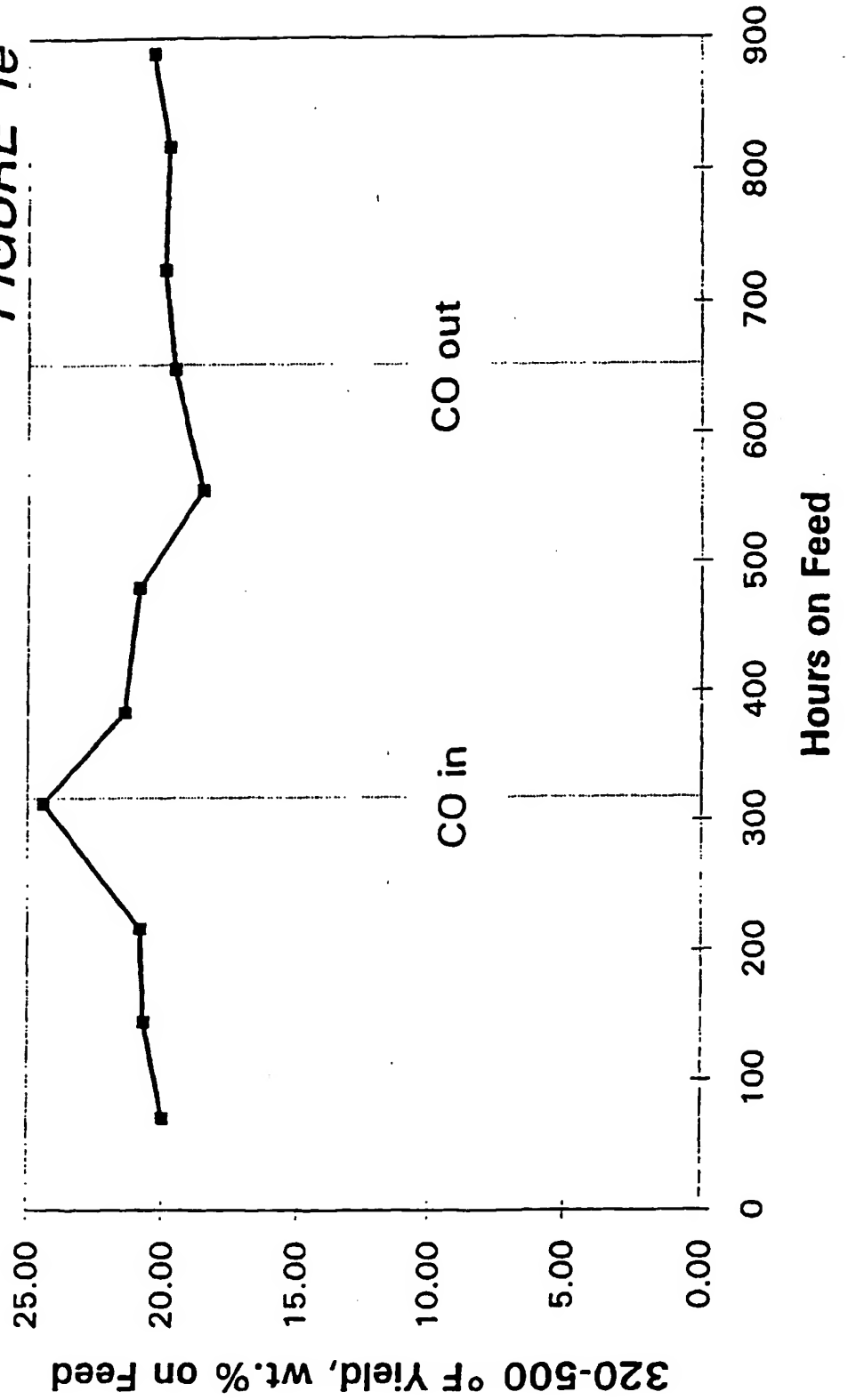

320-500 °F Yield, wt.% on Feed
25.00
20.00
15.00
10.00
5.00
0.00
0
100
200
300
400
500
600
700
800
900
Hours on Feed
CO in
CO out

FIGURE 1f

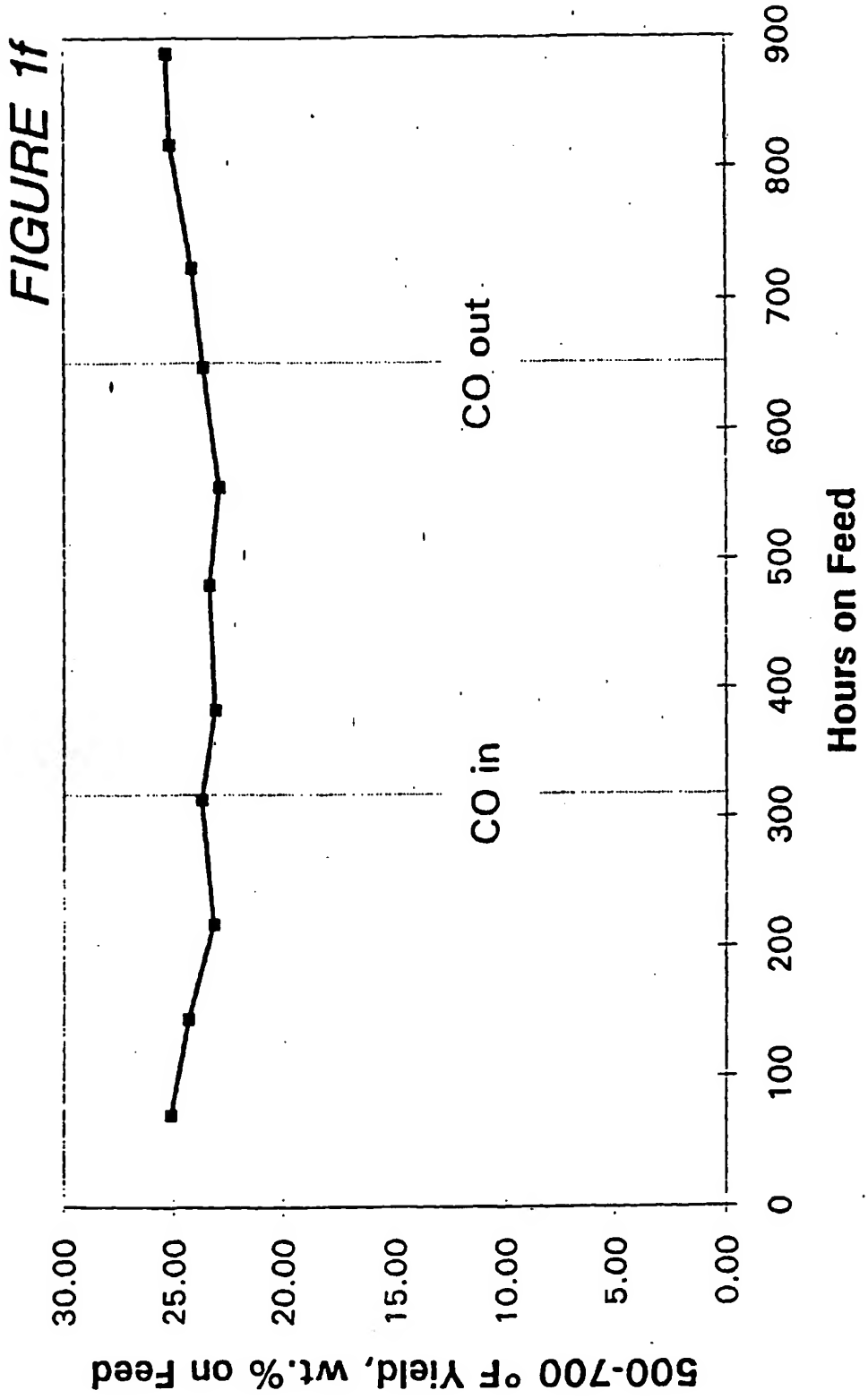

500-700 °F Yield, wt.% on Feed
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0
100
200
300
400
500
600
700
800
900
Hours on Feed
CO in
CO out

FIGURE 2a

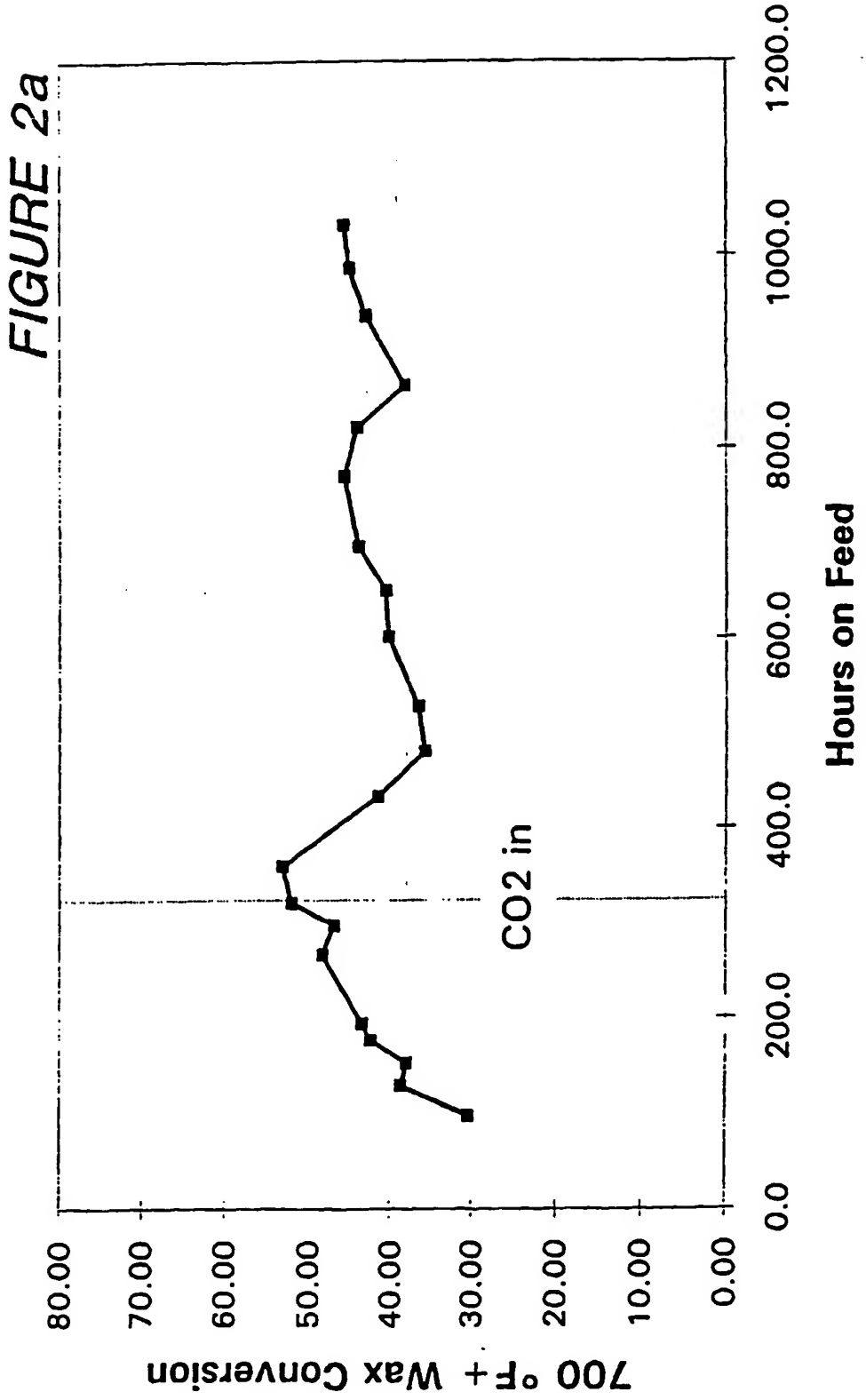

700 °F+ Wax Conversion
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
Hours on Feed
CO2 in

FIGURE 2b

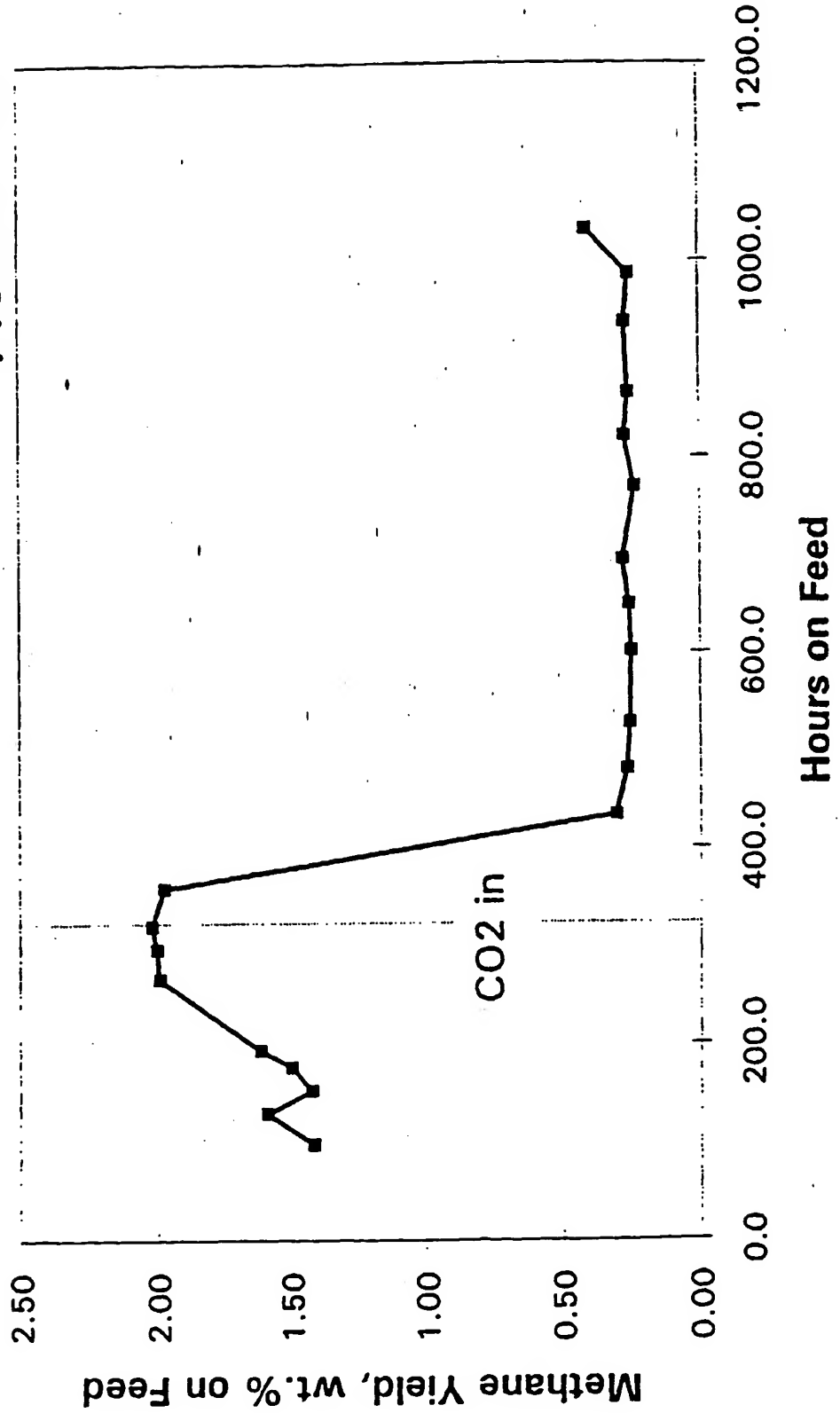

Methane Yield, wt.% on Feed
2.50
2.00
1.50
1.00
0.50
0.00
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
Hours on Feed
CO2 in

FIGURE 2c

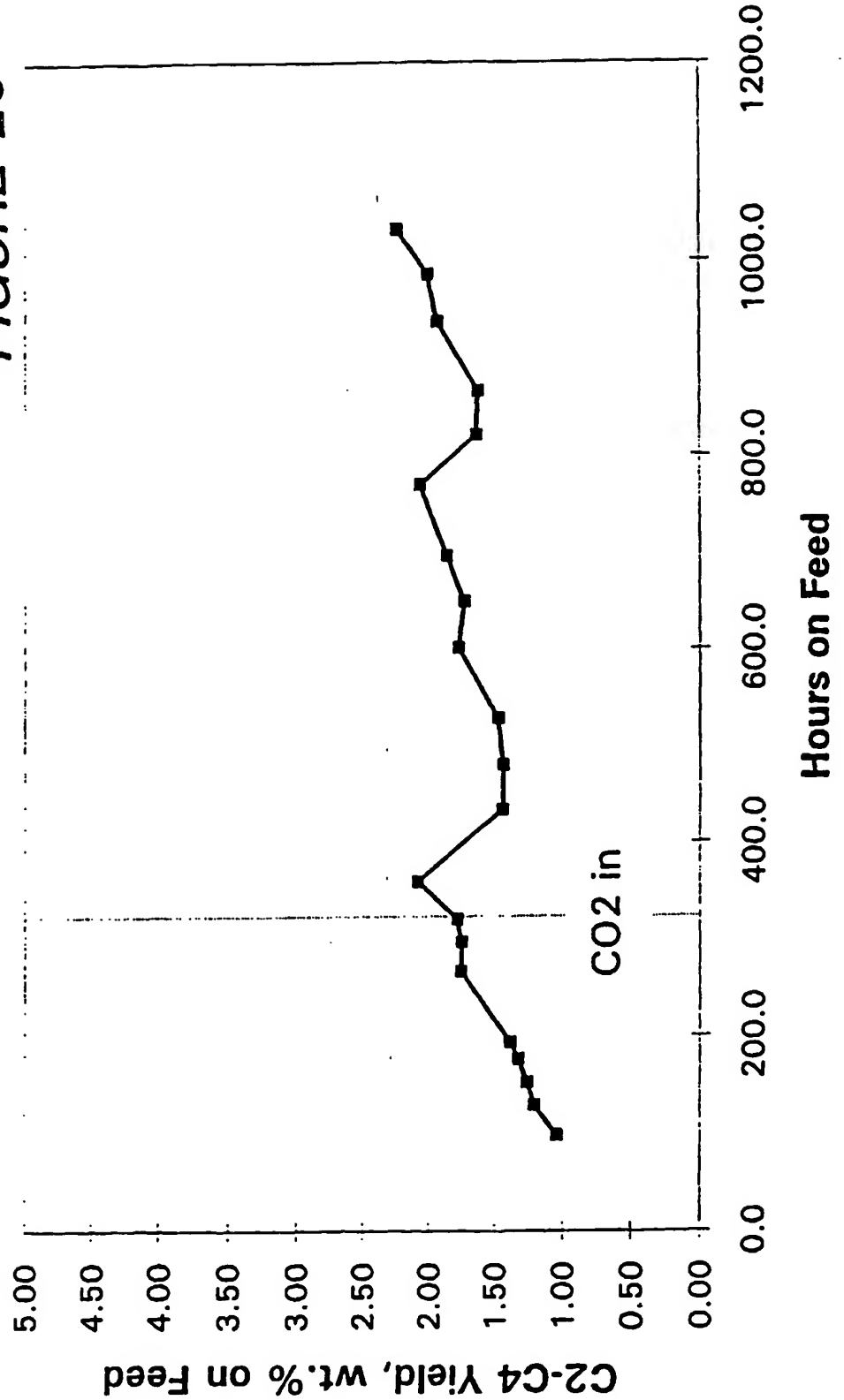

C2-C4 Yield, wt.% on Feed
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
Hours on Feed
CO2 in

FIGURE 2d

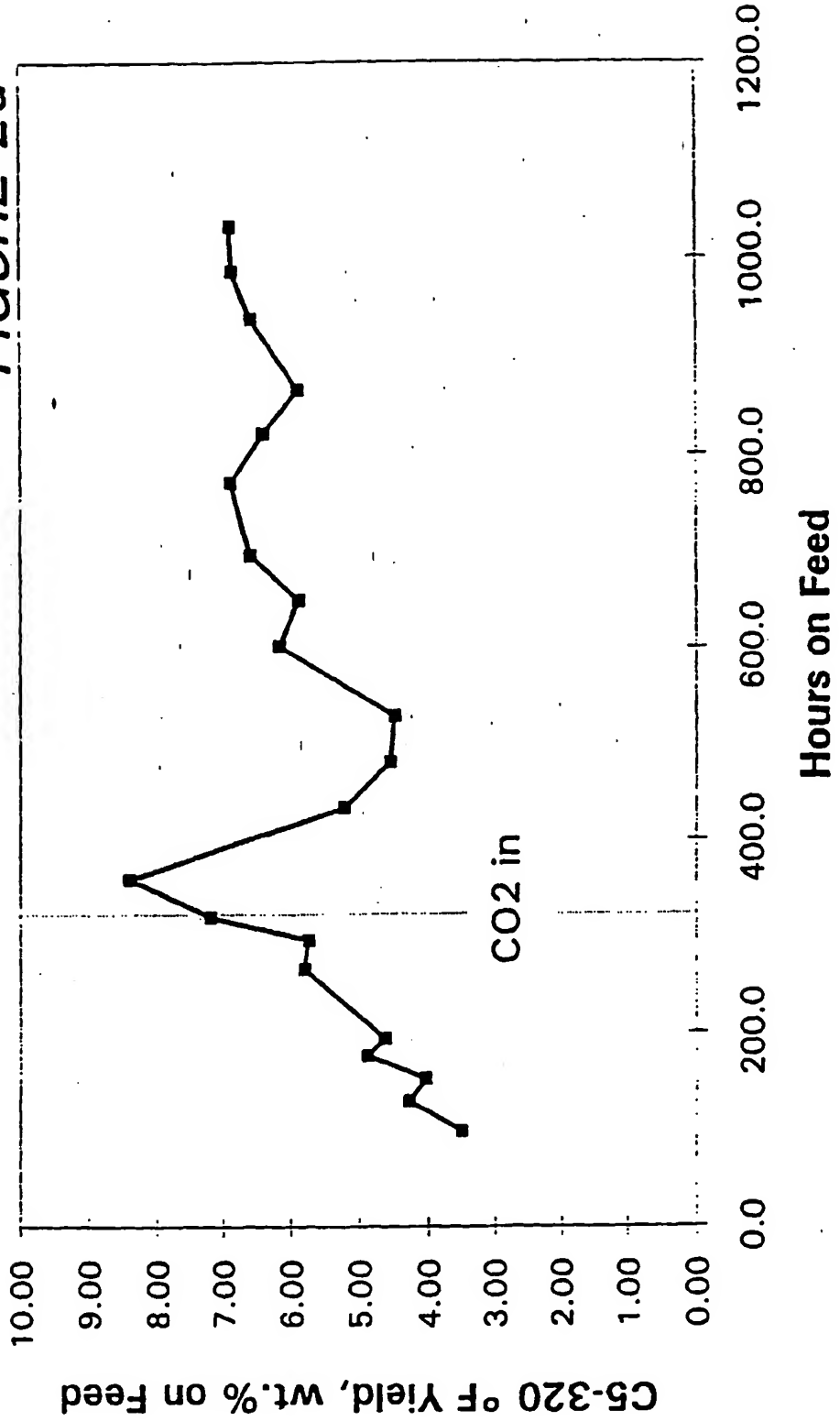

C5-320 °F Yield, wt.% on Feed
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
Hours on Feed
CO2 in

FIGURE 2e

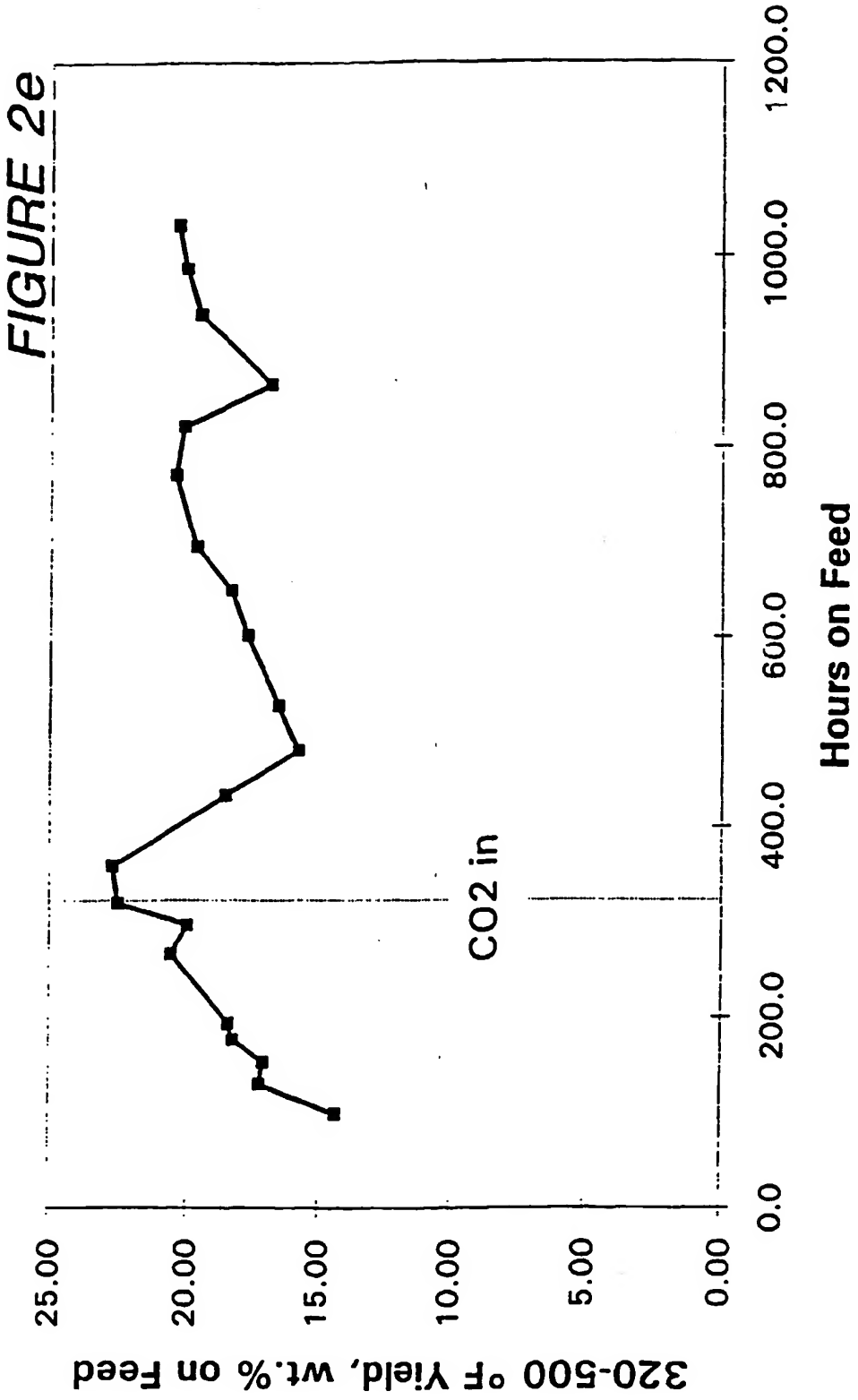
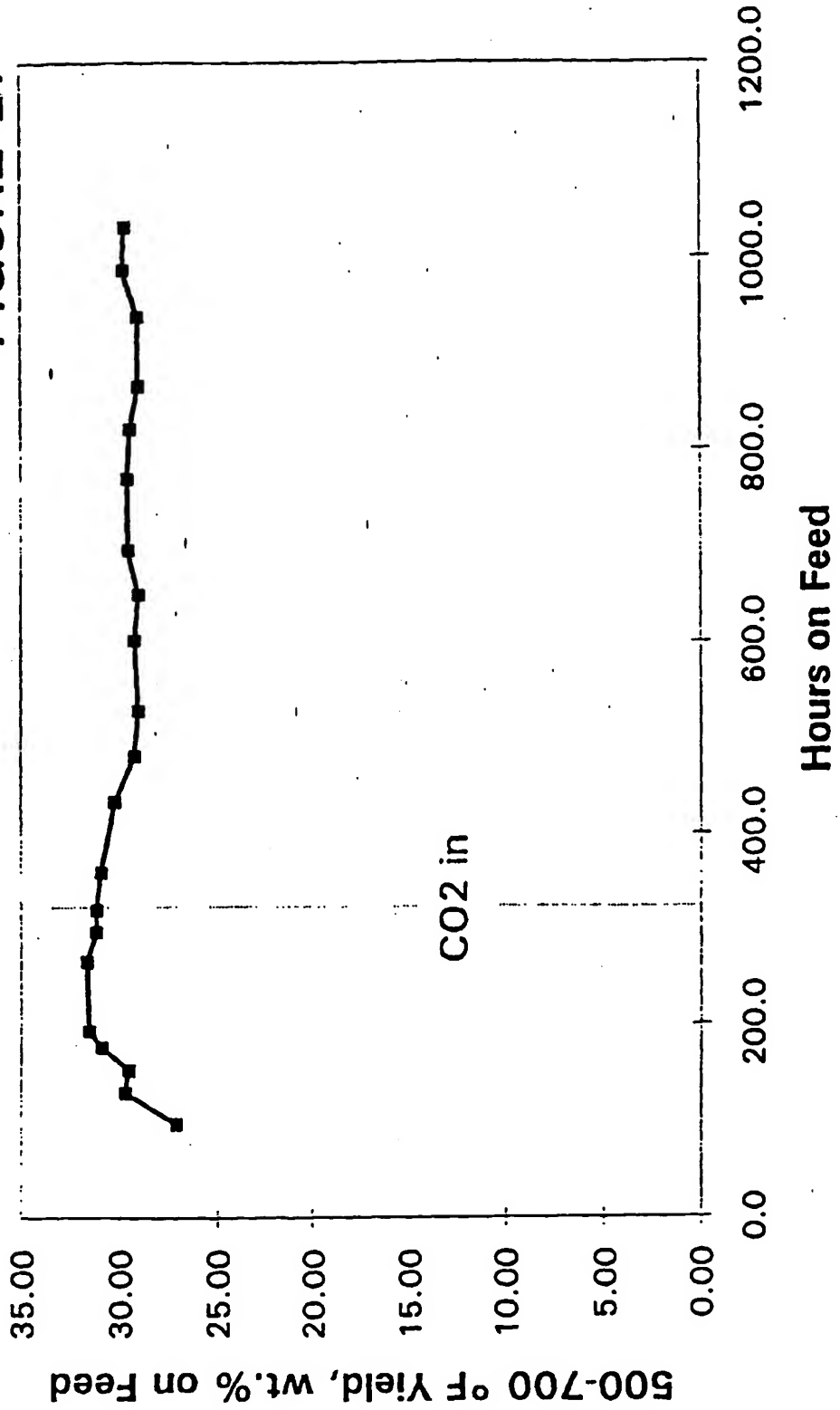

320-500 °F Yield, wt.% on Feed
25.00
20.00
15.00
10.00
5.00
0.00
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
Hours on Feed
CO2 in

FIGURE 2f


500-700 °F Yield, wt.% on Feed
35.00
30.00
25.00
20.00
15.00
10.00
5.00
0.00
0.0
200.0
400.0
600.0
800.0
1000.0
1200.0
Hours on Feed
CO2 in

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☑ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.
As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.